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Review article

Chitosan as an adhesive

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ABSTRACT

Chitosan is a well-known polysaccharide abundantly published during the last decades. This heteropolymer, composed of 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose, is obtained after alkaline deacetylation of chitin from crustaceans, fungi and other non-vegetable organisms. Soluble only at acidic pH, it is the unique polycationic polysaccharide extracted from bioresources. This characteristic gives to it original and specific properties finding some applications in several industrial fields but especially in the biomedical one because of its biocompatibility and its non-toxicity. Besides these traditional applications other ones begin actually to appear in the literature. They focus on the development of chitosan-based adhesives, binders or films. This review synthetizes the state of the art on this domain, but also deals with the assessment of chitosan environmental impact.

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Contents

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1. Introduction

Chitin, deacetylated chitin (chitosan) and their derivatives are probably in the top 3 of the more published polysaccharides in the scientific literature, with cellulose and starch. This "old polysaccharide" sometimes called "animal cellulose" has also interested the field of industrial applications as a simple research in web site of the European Patent Office using the term "chitosan" finds 16,300 patents. However, despite this abundant literature and activity of patent deposition, chitin and chitosan have not known the same commercial success than cellulose even if these two polysaccharides are in competition for the most abundant natural organic compound on earth. The explanation could be in the structure of chitin which has some specificity compared to cellulose even if these two polysaccharides have basically a similar arrangement pattern. They are high molecular weight polymers of glucose linked by β-(1,4) glycosidic linkages. However, in the case of chitin, acetamido groups replace hydroxyl ones on the C-2 of glucose units leading to a polymer of N-acetyl glucosamines. The oxygen of this acetamido group can form hydrogen bonds with adjacent —NH or —OH functions reinforcing the insolubility of chitin. So, the degree of N-acetylation, i.e. the ratio of 2-acetamido-2-deoxy-D-glucopyranose to 2-amino-2-deoxy-D-glucopyranose structural units has a striking effect on chitin insolubility and limits its swelling possibilities in water compared to cellulose [153]. This main difference between these two polysaccharides can explain why the evolution has done the choice to conserve them for the same biological function, meaning the mechanical resistance and tissue isolation of organisms. Cellulose has been selected by plants which have to conserve some degrees of interactions with water, notably during the growth of their tissues, whereas chitin is employed by some marine organisms and insects which have to build an impermeable exosqueleton. Fungi have not done any choice having cell-walls with chitin and cellulose. Chitosan obtained after alkali deacetylation of chitin exhibit rates of deacetylation higher to 50% and can easily form quaternary nitrogen salts at low pH values where it is soluble. The expensive production of chitin and chitosan from marine organisms compared to cellulose obtained from terrestrial plants is probably at the origin of their under exploitation despite their huge potential. Current applications are usually concentrate on the biomedical fields such as tissue engineering, gene vectors, and drug carriers [43,187]. However, the increase of commercial availability of chitosans open the way to the development of materials notably in the field of films, binders and adhesives [50,142,153,176]. Most adhesives *viz.* polyvinyl acetate, epoxy adhesives, phenol/formaldehyde and polyurethane depend on non-renewable and depleting petrochemical resources. Moreover, numerous adhesives, films and binders are prepared with residual toxic chemicals, such as formaldehyde and Volatile Organic Compounds (VOCs) that are injurious to health and environment [142]. The development of natural and renewable molecules exhibiting good bonding properties is actually an industrial challenge. The bio-based polymers need to match the properties of conventional compounds and/or introduce new valuable properties, preferably without any cost increase. Protein, tannin, lignin, and polysaccharides are examples of interesting bio-based polymers that have been suggested as good candidates for adhesives and binders developments [154]. Among them polysaccharides such as chitosan are an interesting group of polymers. Their numerous hydroxyl groups can interact with à lot of chemical functions and their high molar mass allows cohesive strength to materials. One of advantage of chitosan is its insolubility at neutral pH and its solubility at acidic ones. The combination of all these characteristics with its good mechanical properties, its biocompatibility and its biodegradability open the way to a lot of original applications in the adhesive and binder area. Note also that recently developed chitosan based nanomaterials have superior physical and chemical properties such as high surface area, porosity, tensile strength, conductivity, photoluminescent as well as increased mechanical properties compared to pure chitosan [182]. It appears then that a consolidation of data relating to this subject is required.

2. Chitosan: from the source to its characteristics

2.1. Origin

Chitin was the first polysaccharide identified by man from mushrooms preceding cellulose by 30 years [23,102]. After that this polymer was identified in the shells of insects and the exoskeletons of molluscs combined with minerals and proteins to harden these structures by cross-linking with polyphenols. In 1859, C. Rouget subjected first chitin to alkali treatment, which resulted in a substance that could be dissolved in acids. In 1894, the term "chitosan" was given to this deacetylated chitin by Hoppe-Seiler [187].

2.2. Structure

Chitins can be divided into α-, β-, and γ-chitins due to hydrogen bonds in their structures. α-Chitin comprises
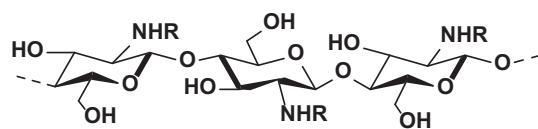

(With R= H or COCH$_3$)

Fig. 1. Chemical structure of chitosan (%COCH$_3$ ⩽ 40%).

two antiparallel polysaccharide chains and β-chitin two parallel ones. γ-Chitin is composed of three parallel polysaccharide chains, two of which being in the same direction. α-chitin is the most stable one and the other two types can transform into α-chitin if conditions permit. Different configurations lead to different functions. α-Chitin with high hardness can be found in rigid parts of some organisms such as sellfish exosqueletons. It is and usually combines with shell protein or inorganic compounds. γ- and β-Chitins, more flexible are find in soft and firm parts of some animals such as squid pens [187]. Chitosan is a biosourced polysaccharide obtained by alkaline deacetylation of chitin [50]. It is a heteropolymer of β-(1,4)-linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose (Fig. 1). In the commercial and scientific areas, the term "chitosan" is usually attributed to products of chitin with over 60% deacetylation degree and nitrogen content higher than 7%. This macromolecule is a primary aliphatic amine and is the sole cationic polysaccharide due to its positive charges (NH_3^+) at acidic pH (pH < 6.5) [15,160]. Therefore, chitosan can be protonated by selected acids such as: formic, acetic, lactic, malic and citric acids. Generally, chitosan is described in terms of degree of deacetylation (DD) and average molecular weight (Mw) [50,132,131].

2.3. Processes for chitosan production

It is estimated that approximately 10 billion tons of chitin can be synthesized in nature each year [187]. The main sources of chitin (in% of dry matter) are crustaceans such as shrimp and crab (58–85%), insects (20–60%), molluscs (3–26%); cephalopods including squids, octopuses and annelids (20–28%), protozoans which contain a little chitin, coelenterates (3–30%), seaweed which can contain low quantities of chitin and fungi whose chitin contents are from trace to 45%.

2.3.1. Extraction from crustaceans

Crustacean shell waste is the richest source of chitin available with enough quantities to support a commercial chitin/chitosan industry. The method usually used for the isolation of chitin from crustacean shell consists of three steps: deproteinization, demineralization and decolorization [26,80,175,65]. After that, chitin is deacetylated to make chitosan or other products for a wide array of applications. The process of chitosan production is summarized in Fig. 2. A detailed review of the different chemical extraction methods of chitin from shellfish waste employed between 1954 and 1993 was performed by No and Meyers [137]. Similarly, various methods for demineralization and deproteinization of chitin from Hariana Shrimp (*Metapenaeus monoceros*) shells were examined by Naznin [134]. Independently of starting materials, proteins are first removed from shells by treating them with mild sodium hydroxide or potassium hydroxide solutions (between 1% and 10% w/v) at temperatures ranging from 30 °C to 100 °C for 30 min to 12 h. The optimal method for the deproteinization of crab and shrimp shells (removal of proteins superior to 90%) was reported for treatments with 1–2% KOH at 90 °C with a shell to alkali solution ratio of 1:20 (w/v) during periods between 1 and 2 h [175]. Calcium carbonate, calcium phosphate, and other mineral salts found in shell waste are then extracted with dilute acids [137]. Recently, Hajji et al. [65] have shown that α and β-chitins were extracted by treatment with dilute HCl solution for demineralization followed by enzymatic deproteinization using protease from *B. mojavensis* A21. High demineralization and deproteinization rates were achieved by these treatments. Finally, the removal of acetyl groups of chitin to obtain chitosan is done using a harsh treatment usually performed with concentrated alkali solutions (NaOH or KOH). The amount of NaOH (or KOH) represents an economic and ecological worry in this process [171,90]. Therefore alternatives are being sought to keep the NaOH to a minimum. For this, chitin is mixed with NaOH powder (weight ratio 1:5) by extrusion at 180 °C. Highly deacetylated and soluble chitosan is then obtained with just one half of the NaOH needed for aqueous systems.
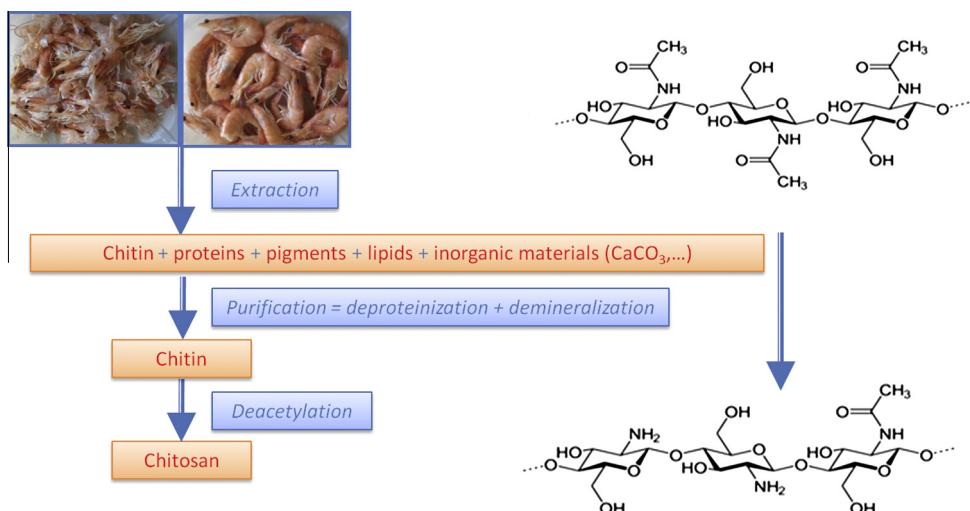

Fig. 2. Process for the production of chitosan from crustacean shell waste.

It is possible to extract chitin/chitosan from other resources such insect's cuticles and fungi. However the utilization of those sources (even if they remained available sources) is not really competitive compare to crustacean shells or squid pens. Commercial chitin/chitosan industries from the insects/fungi remain expensive nowadays but the chitosan extracted from those sources is of high quality and find some specific bio-applications.

2.3.2. Extraction from insects

Insect cuticle is composed of chitin, melanin, and proteins, of which protein and melanin are alkalisoluble [135,140]. The procedure for extraction of chitin and chitosan from the cuticle of insects is similar to that of crustacean sources [64,206,135,147]. Their demineralization is stronger than the demineralization process of aquatic crustacean materials [161]. Zhang et al. [206] found that the crystallinity of chitin increased and 55% of the N-acetyl groups of silkworm chitin were removed after treatment with 2 M HCl at 100 °C. Therefore, the treatment of insect cuticle with dilute HCl has a double functionality: removal of mineral and acetyl groups of insect chitin. After this acidic treatment, the chitin was washed with Na_2CO_3 at 0.4% (w/v) for 20 h to completely remove the proteins. The total deacetylation of insect chitin was then carried out by using NaOH (10–12.5 M) for 15–16 h at 110 °C–150 °C. Paulino et al. [147] obtained chitin with high purity from silkworm pupa, but the yields were low comparing with those of chitin and chitosan produced from aquatic crustacean shells. Haga [64] and Nemtsev et al. [135] have used decolorization agents to remove pigments from chitin of silkworm pupa and bee corpses. Nemtsev et al. [135] observed that melanins were absent in the bee chitin after treatment with hydrogen peroxide. This chitin was then called "white chitin". In general, the degree of deacetylation of insect chitosan is about 70–95%.

2.3.3. Extraction from fungi

The extractions of chitin and chitosan from different species of fungi such as *Agaricus bisporus*, *Auricularia auriculajudae*, *Lentinula edodes* and *Pleurotus sajor-caju*, have been reported in some publications [155,205,127]. The total yields of chitin and chitosan from these species were around 85–196 and 10–40 mg/g of dried biomass respectively [155,205,127]. The processes for the extraction of chitin and chitosan from *Lentinus edodes* were nearly the same for Crestini et al. [41] and Pochanavanich and Suntornsuk [155]. The authors used 1 M NaOH at 121 °C for 0.25 h for deproteinization and the chitosan was extracted from the alkaline insoluble material using 2% acetic acid at 95 °C for 8–14 h. Mario et al. [127] used 1 M NaOH at 40 °C for 15–17 h for deproteinization and the chitosan was extracted from the alkaline insoluble material using 5% acetic acid at 90 °C for 3 h. However, Yen and Mau [204] extracted chitin from shiitake stipes using alkaline decolorization treatments and then deacetylated it with concentrated NaOH solution to obtain chitosan. In their method they did not purify the chitosan using acid extraction process. The yield of extracted chitosan depends on mushroom species, harvesting time, processes and physico-chemical conditions of extraction

[155,204]. From the literature, it can be considered that the major problem in the extraction of chitosan from mushroom is that chitin/chitosan is complexed with glucans or other polysaccharides. Consequently, the extraction of chitin and chitosan is difficult and the yields are low. Fungal chitosans have a degree of deacetylation of 70–90% and an average molecular weight about 1–2×10^5 Da depending on mushroom species and treatment conditions [41,155,204,127]. In comparison with conventional natural fibers, fungal filaments have the advantage that different kinds of filamentous structures are available, ranging from straight fibers several centimeters in length (sporangiophores) to branched microscopic filaments (mycelium). The mycelium of basidiomycetes can be considered as an alternative source for the production of chitin and chitosan that might be useful for some specific practical applications. Indeed, chitin-based filamental structure can be applied directly for many biomedical and pharmaceutical applications [73,169].

2.3.4. Effects of the production method on chitosan characteristics

Treatment of extraction and deacetylation can affect the characteristic of chitosans, namely average molecular weight (Mw), degree of deacetylation (DD), crystallinity, presence of reactive terminal groups, viscosity of solutions, purity, color, clarity, consistency and uniformity. Higher temperatures reduced the Mw of the resultant chitosans [119]. DD is the most important parameter affecting potential industrial applications of chitin and chitosan. In fact, it controls the solubility, the chemical reactivity during chemical modifications and the biodegradability. Depending on the source and the preparation procedure, DD may range from 5% to 60%. Hence, different values of DD lead to different physico-chemical properties and different solubilities [196,65,193].

Another method that requires considerably less severe conditions and resulted in better deacetylation with less degradation was described by Domard and Rinaudo [47] who added thiophenol as an oxygen trap and catalyst. Here, deacetylation took place using a calculated four times excess of NaOH for the total N-deacetylation of all amino groups in chitin (concentration range 2% (w/v)). Reaction time was 1 h at a temperature of 100 °C. The technique was later refined by Suryanarayana Rao et al. [184] who impregnated chitin with a four times excess NaOH (w/v) by mixing and heating at 60 °C for 2 h. This was clearly demonstrated by Kurita et al. [100] who obtained 70% DD from squid pen β-chitin compared to only 20% using shrimp shell α-chitin using 30% NaOH at 100 °C for 2 h. Conversely, chitosan with a degree of deacetylation of 90% was obtained from squid pens after autoclaving for 15 min [2]. No et al. [138] eliminated the deproteinization step and reduced the treatment time with alkali to examine their effects on the physiochemical and functional properties of chitosan. Results showed that chitosan had a higher Mw and viscosity, a lower DD, lower solubility and reduced water and fat-binding capacity when compared to chitosan obtained by traditional methods. Hajji et al. [65] have extracted chitosans from shrimp (*P. mediterraneus*) waste after strong alkaline conditions giving degree of

acetylation lower than 20% but low viscometric-average molar mass.

The chitin deacetylase could replace usefully the hot concentrated alkali treatment of deacetylation preventing serious environmental pollution, lowers energy consumption, and solves the problem that product treated with hot concentrated alkali has uneven DD and low relative molecular weight. The product formed by the enzyme method can be used for producing new functional materials. Nevertheless, there are still some problems such as low yields of deacetylase-producing strains and low enzyme activity. Moreover, natural chitins are crystals, not a good substrate for deacetylase. Hence, many preparations still need to be carried out before the chitin deacetylase method can be used in the industrial production of chitosan [187].

3. What are the mechanisms of adhesion?

Although the adhesion is used for more than 30 centuries, the mechanisms which govern the adhesion between two materials remain complex and partially underestimated [40]. In the aim to understand why the chitosan can be considered as a good adhesive microscopic and macroscopic aspects of the adhesion have to be consider. The adhesive can be considered as liquid before its application and it solidifies in contact of the adherend.

3.1. Theory of adhesion

An adhesive is a material used to link two surfaces with a strong adhesion. Mc Bain and Hopking [128] are the first to propose a theory of adhesion called the "mechanical interlocking model". The adhesion is assured by the penetration of the adhesive in the irregularities, micro-cavities or pores of the surface before solidification. The roughness and the porosity are favorable to the adhesion only if a good wettability exists. Van der Leeden and Frens [194] showed that the shape of asperities had an importance in the adhesion, certain forms not being favorable. The adhesive has to have adequate rheological properties to penetrate into the asperities. Indeed, if the adhesive does not fill completely the asperities, it forms air bubbles which create constraints and weaken the collage. The mechanical interlocking theory is found on porous or rough substrates such as wood, fabrics and paper but some metallic substrates such as anodized aluminum are also a good example [55]. In reality, the mechanical interlocking model does not take into account phenomena which occur at the molecular level on the adhesive/substrate interface.

Mechanisms of adhesion are also governed by adsorption theory. This theory involves interatomic and/or intermolecular forces which are established between the molecules of adhesive and molecule at the surface of the adherend. Kinlock [92] classified the various interactions according to their associated energy (values in brackets). The stronger interactions are covalent (150–950 kJ mol^{-1}) and ionic (400–800 kJ mol^{-1}) bonds compared to van der Waals forces (2–15 kJ mol^{-1}) and hydrogen bonds (10–40 kJ mol^{-1}) [92].

A third theory of adhesion deals with the electrostatic attraction theory. This mechanism is based on the interface between the adhesive and the adherend where a mutual sharing of electrons between the two materials is possible [92]. The adhesive/adherend system is considered as a plan condenser formed by the two electronic layers of both adhesive and adherend surfaces. It develops an electrostatically double layer of ions. The pH of the environment between the adhesive and adherend involves also electrostatic forces depending on the formation of hydrogen bonds between a hydrogen donor and a hydrogen acceptor [56]. The acid can be metallic hydroxide and the base an amine group. For Yang et al. [203], this model is only applicable in the case of incompatible materials such as polymeric and metallic substrates for example.

The diffusion or interdiffusion theory proposed by Voyutskii [197] can be applied only for polymers which are mutually miscible and compatible. The adhesion results from the interdiffusion of the molecules at interfaces [203]. The diffusion is optimal when the solubility characteristics of both polymers are equal [66]. Fick's laws can be applied to this diffusion mechanism. The temperature has also a significant influence on the mobility of the molecules. Maeva et al. [121] concluded that the diffusion model of adhesion can be applied only if the temperature is inferior of the glass transition. However, several studies showed the existence of an interface in the neighborhood of metallic substrates. This interface can be characterized by a gradient of glass temperature between adhesive and adherend [63,162]. Sharpe and Schonhorn [177] introduced the wetting phenomenon in the adhesion mechanism. It is the thermodynamic theory of adhesion. A direct measure of these interatomic or intermolecular forces is the measurement of contact angle between the adhesive and the adherend at the thermodynamical equilibrium. This equilibrium satisfies the Young equation (Eq. (1)).

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \qquad (1)$$

where γ_S is the surface free energy of the solid substrate; γ_L is the surface free energy of the liquid drop; γ_{SL} is the interfacial free energy between the solid substrate and the liquid drop. Surface free energies are expressed in N m^{-1} and θ is the contact angle between solid liquid interface. Smaller is the contact angle better are the wettability and the adhesiveness. In principle, the Young's equation applies only to one-dimension spreading and becomes invalid if the substrate is not rigid and motion of the contact-lines takes places in both horizontal and vertical directions [14]. In numerous cases, the roughness of surface and impurities provoke a deviation of the contact angle compared with the contact angle predicted by the Young's equation.

3.2. How to characterize the adhesion?

The fracture between two pieces of adherends bind by an adhesive is initially provoked by a crack or a default. There are three ways of applying a force to enable a crack (Fig. 3)

Mode I: crack-Opening   Mode II: Forward-shear   Mode III: Scissor-shear
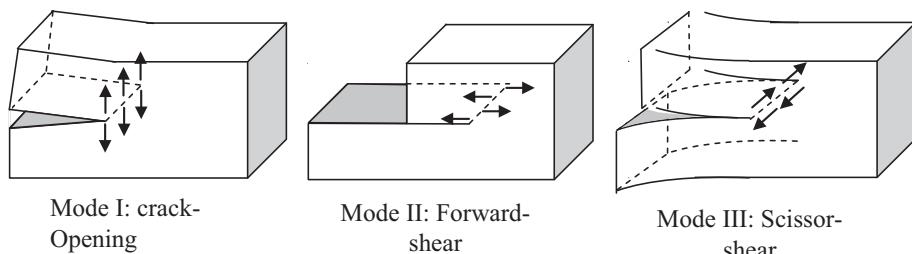
Fig. 3. The three fracture modes.

– mode I fracture: opening mode (a tensile stress normal to the plane of the crack),
– mode II fracture: sliding mode (a shear stress acting parallel to the plane of the crack and perpendicular to the crack front),
– mode III fracture: tearing mode (a shear stress acting parallel to the plane of the crack and parallel to the crack front).

In the case of adhesive system, we can distinguish various modes of break according to the place where the crack takes place.

– The crack is on one of the substrates or on the adhesive: it's the cohesive failure. The adhesion between the constituents is the strongest.
– The crack is at the interface: it's the adhesive failure.
– The crack can be mixed: cohesive and adhesive failure.

Shear loaded joints are the most popular because most of the bonded configurations induce shear failure in the bonded joints [168]. There exists different tests: single lap shear test [60,82,83,189] or cleavage tests [6,30] well described in literature.

4. Chitosan as adhesive: physicochemical characteristics

A liquid adhesive is characterized by three values: the surface tension, the viscosity and the penetration of the adhesive on the material support. The surface tension is a property of the surface of a liquid that allows it to resist an external force. The viscosity of a fluid is a measure of its resistance to gradual deformation i.e. the resistance in the spreading.

The adhesive surface tension must be inferior or equal at the material surface energy to obtain a good molecular interaction. Metals have high surface tensions: 1134 mN m^{-1} for Al and 2266 mN m^{-1} for Fe [8]. Polymers have lower surface tension: 35.76 mN m^{-1} for polyethylene for example [99]. Kutnar et al. [101] estimated that surface tension of viscoelastic thermal compressed wood is ranged between 28.6 and 35.5 mN m^{-1}. Chitosan at low concentration (0.5% w/v) has surface tension of 64 mN m^{-1} at $t = 0$ (initial time) which decreases to 41 mN m^{-1} after a long time [193]. The surface tension reduction could be attributed to the cooperative effect of protein contamination of industrial chitosan [28]. Solutions of chitosan with more important concentrations

have lower surface tensions. For example a solution of chitosan at 2% (w/v) in 2% acetic acid (v/v) exhibited a surface tension of 37.4 mN m^{-1} [163]. Kurek et al. [99] have determined for chitosan 2% (w/v) in 1% (v/v) acetic acid a dispersive part of 38.59 mN m^{-1} and a polar part of 1.10 mN m^{-1}. It means that acid-base interactions of Lewis were dominating. Chitosan favors the collage with materials of low surface energy. Furthermore a low surface tension and a high dispersive part indicate that chitosan easily spreads out on almost every type of materials. Chitosan solution exhibits Newtonian behavior at concentration lower than 0.25% (w/v). Above this value, chitosan solution has shear-thinning behavior [28]. The viscosity of chitosan solution increased with concentration but decreased with temperature [35]. Mati-Baouche et al. [126] obtained a viscosity of 90.2 Pa s for chitosan solution at 4% (w/v) and 7132 Pa s for a solution at 9% (w/v) at 25 °C. Note that Bajaj et al. [13] showed that deproteinization and deacetylation conditions applied to chitosan influence its viscosity in solutions. Umemura et al. [192] compared the viscosity of chitosan solution with different molecular weights: it varies of 3.2 Pa s^{-1} in 1085 Pa s^{-1} respectively for chitosan 35 kDa and 350 kDa. This large range of viscosity is an advantage in the use of chitosan as adhesive. The viscosities of classical and synthetic adhesives, such as phenol–formaldehyde adhesive solutions, are ranging between 60 and 2 825 MPa s [79] and those of various solutions of biosourced polysaccharides with adhesive properties are from 40 to 400 Pa s (xanthan gum, guar gum and locust bean gum) [139]. The value of the adhesive viscosity depends of the application [27] and chitosan viscosity can be easily adapted. The penetration of chitosan solutions into porous adherend materials is discussed only by Patel et al. [144] and Mati-Baouche et al. [125]. After microscopic observations, they proved there is no penetration of chitosan into wood [144] and into sunflowers [125]. Porosities of wood or other lignocellulosic materials are very small (some microns). Normally, the roughness of surfaces of adherends are of an upper order compared to this porosity. So, the low surface tension of chitosan solutions and an adapted viscosity allow penetrating well into these asperities. Note also that positively charged chitosan (acidic pH) in wet conditions interact strongly with negatively charged surface via electrostatic forces but also via hydrogen bonds and van der Waals forces between D-glucosamine and hydrated surface or adherend [113]. The same authors described also strong cohesive strength between two opposed chitosan films (wet conditions) in acidic buffer and explained

them by the formation of hydrogen bonds enhanced by structural changes in the chitosan molecules from a relaxed 2-fold helix to an extended 2-fold helix due to the confinement of the chitosan films during contact. Once dried, the adhesive has to possess good mechanical properties (traction resistance, shear resistance, etc.) and resist to outside attacks (water, temperature, etc.). The Table 1 gives the mechanical properties of some chitosan films. Park et al. [145] studied tensile stress of films prepared with 3 chitosan molecular weights and 4 organic acid solvents. Tensile strength (TS) varied widely ranging from 7 to 150 MPa depending on both the molecular weight (Mw) of chitosan and the type of acid used to solubilize it [146]. In the same time, elongation at break varied ranging from 4.1% to 117%. The highest TS (150 MPa) was observed for a 92 kDa chitosan solution at 2% (w/v) in acetic acid 2% (v/v) whereas the best value of elongation at break (117%) was obtained with a solution of 37 kDa chitosan at 2% (w/v) in a 2% (w/v) citric acid solution. These differences can be explained by the ratio of hydrogen bonds between hydroxyl and amino groups in chitosan films [193]. Mati-Baouche et al. [126] obtained elastic modulus for chitosan films ranged between 2.5 and 4 GPa. The mechanical behavior can be modified by addition of plasticizer. Plasticizers are additives used to increase the elasticity of polymers and give to them a higher resistance to mechanical constraints. The main plasticizers described in literature are polyethylene–glycol (PEG) [4,120], glycerol [22] and sorbitol or saccharose [11]. The shear resistance of chitosan adhesive was measured by Patel et al. [143] on aluminum and wooden assemblies. It was tested with double-lap-bonded specimens for aluminum [143]. The shear strength obtained with solutions of chitosan 6% (w/v) in acetic acid 2% (v/v) was ranged between 6.9 MPa and 27.2 MPa depending on surface treatment applied to adherend. The shear strength can reach 40.8 MPa for solutions of chitosan 7% (w/v) in acetic acid 2% (v/v) supplemented with glycerol 1% (v/v). For wooden assemblies, Patel et al. [144] tested different solutions of chitosan using double-lap shear tests (4% (w/v), 6% (w/v) and 6% (w/v) supplemented by glycerol 1% (v/v) and trisodium citrate 5 mmol L^{-1}). The strength at beak varied between 4.2 and 6.4 MPa and 80–90% of the specimens exhibited a cohesive failure. It means that the adhesive interface is stronger than the wood. Other authors have tested adhesives with wooden assemblies. Shear resistance of plywood with Urea Formaldehyde (UF)-Glutaraldehyde adhesive is tested by Maminski et al. [122]. The value of the strength at break depends on the nature of the wood

but it does not exceed 2.7 MPa. Umemura et al. [190] obtained the same results with UF resin, casein and soybean glues using peel tests and 0–30% of the specimen exhibit a cohesive failure. In comparison, chitosan can be considering as a good adhesive. Umemura et al. [190] estimated the water resistance of chitosan on plywood adherends after 24 h water soaking. The bond strength was 2.13 MPa for dried specimens with 20% wood failure whereas the bonded resistance was 1.4 MPa for wet specimens with 0% wood failure. The bond strength after water immersion treatment was inferior to that of UF resin adhesive (2.1 MPa, 30% wood failure). However, compared to biosourced adhesive (the casein and soybean glues), chitosan developed excellent bonding properties [190]. Two values allow characterizing adhesive thermal resistance: glass transition temperature and temperature of decomposition. Glass transition temperature (T_g) represents the transition between solid and viscous phases for polymers. The value is a subject of controversies because concentration, origin, molecular weight, deacetylation degree and crystallinity of chitosan modify the T_g [16]. However, several authors find T_g values ranged between 103 °C [34] and 140–150 °C [48]. Thermal degradation takes place at 250 °C [190,193]. It means that chitosan adhesive can be used in temperatures above the room temperature without any problem until 80–90 °C.

Concerning the quantity of adhesive to be used, Umemura et al. [190] showed that the solid based spread rate of chitosan (16 g m^{-2}) is lower than those of UF-resin adhesive (74 g m^{-2}), of casein glue (67 g m^{-2}) or soybean glue (50 g m^{-2}).

5. Applications of chitosan as adhesive

Applications of chitosan as adhesive can be divided into two groups: biomedical adhesives, which are widely described, chitosan based material adhesive and the adhesive role of chitosan between metallic surfaces.

5.1. Chitosan as biomedical adhesive or bioadhesive

Bioadhesives are high molecular weight, biocompatible, biodegradable polymers used to join two surfaces where at least one of them is a living tissue. Bioadhesives are used for two main purposes, suture-less surgery and substitute for traditional drug delivery systems [84]. One of the first application of chitosan in biomedical field is correlated to its natural hemostatic properties [174]. Thanks to this, it is possible to use chitosan-based material for emergency hemostasis as well as for skin wound closure. This wound closure ability is related to the fact that the chitosan is an excellent muco-adhesive in its swollen state and a natural bio-adhesive polymer that can adhere to hard and soft tissues [43]. Chitosan films are very good biomaterials for wound-healing and tissue repair [31,78,17]. Once placed on the wound, they adhere to fibroblasts and favor the proliferation of keratinocytes and thereby epidermal regeneration. Moreover, on contact with anionic erythrocytes, the chitosan salts rapidly adhere with the wound surface. This adhesive process is thought to be the primary mechanism of action; independent of platelets or clotting factors [21].

Table 1
Mechanical properties of chitosan films. Tensile Strength TS, Elongation at break ε and elastic modulus E.

TS (MPa)	ε (%)	E (MPa)	Chitosan film preparation	References
7.85	65	9.62	2%w/v – 2% lactic acid	[87]
26	33.3	–	2%w/v – 1% lactic acid	[202]
45	11	2500	9%w/v – 2% acetic acid	[126]
61	5	–	1%w/v – 1% acetic acid	[110,111]
71	5	4000	4%w/v – 2% acetic acid	[126]
71.67	14.32	2100	1%w/v – 98% acetic acid	[114]

Recent works have evaluated with success chitosan-patches infused with indocyanine green in association with laser-based repairing techniques to standard suturing in microsurgery [51]. Results demonstrated the efficacy of this technique for the *in vivo* repairing of microvascular lesions and end to end anastomoses. In the same way, Photochemical-tissue-bonding (PTB) using rose Bengal integrated into a chitosan bioadhesive was described as an alternative nerve repair device that removes the need for sutures [107,18]. Photochemical tissue bonding (PTB) is a sutureless technique achieved by applying a solution of rose bengal between two tissue edges. These are then irradiated by a laser that is selectively absorbed by the rose bengal. The resulting photochemical reactions supposedly crosslinked the collagen fibers in the tissue with minimal heat production [109]. Some commercial applications of the adhesive properties of chitosan are already sold, such as Surgilux, a chitosan based laser activated thin film surgical adhesive [53], Hem Con ^{TM} which combines a more than 75% deacetylated chitosan acetate salt on a sterile foam backing pad [52,129,156,199,24], Chitoflex® which is a double sided flexible roll of chitosan [62,181], or Celox^{TM}, a gauze preparation where the cationic chitosan salts produce an adherend seal around the severed vessel surface [95,96,85,94]. Chitosan can also be used in tissue engineering. One impressive example of chitosan use in tissue engineering is described in the article of Chen et al. [33]. In this work, chitosan was combined to genipin or epoxy as crosslinker and compared to metal to build stent. The results indicated that the cyclic crosslinking structures formed within the genipin stent matrix were beneficiary to the improvement of chitosan mechanical properties. The cytotoxicity of the genipin stent was significantly lower than the epoxy stent. Moreover this work explores another huge application of chitosan which is the drug delivery ability. The general procedure involves different configuration of chitosan materials (film, scaffold, foam, etc.) [7]. Thus, illuminating films of porous chitosan matrix supplemented with gold nanorods and thermosensitive micelles loaded with a compound stimulated local photothermal conversion of the gold nanorods. The heat generated led to the ejection of the chemical from the micelles and to the permeabilization of adjacent cell membranes, resulting in a selective cellular uptake of the released chemical [124]. Finally the last subdivision of muco-adhesive chitosan and chitosan based nanomaterials are represented by their ability to generate hydrogels [182,10]. Hydrogels are a network of polymer chains that are hydrophilic; sometimes existing as a colloid gels in which water is the dispersion medium. Hydrogels of chitosan are commonly used as a sealant for wound healing. These gels are obtained with crosslinking agents, such as genipin, polypeptides or enzymes. As example, a thiol-modified chitosan was *in situ* crosslinked by an efficient polypeptide crosslinker in the work of Nie et al. [136]. This crosslinker was obtained by the reaction of maleimide groups onto polylysine and the final hydrogel adhesive sealant showed an adhesion strength 4 times higher than that of the commercial fibrin glue. It is notable to observe that chitosan is also able to form a gel, without any additive. The mechanism of this gelation is based on the neutralization of $-NH_2$ groups to block the repulsion between chitosan chains thus resulting in the formation of hydrogels through hydrophobic interactions, chitosan crystallinity and hydrogen bonding. Thanks to its polycationic nature, chitosan in acidic medium with polyanions forms hydrogels via electrostatic interaction [43,103]. To sum up, chitosan is a good mucoadhesive widely used for this property in several applications which are summarized in Table 2 [49].

The major application of chitosan is related to bioadhesion, but some other works described more particular applications of chitosan as adhesive.

5.2. Other adhesive applications of chitosan

Referring to the literature, chitosan is a performing wood adhesive. In the study of Ibrahim et al. [74], laccase modified lignin was reacted with chitosan to formulate resins that are safe and cheap, and the formulations were tested for their adhesive properties on wood joints. The strength of lignin-chitosan was higher than unblended lignin and similar to lignin blend with soy protein and polyethylenimine. To the same end, Peshkova and Li [148] have developed chitosan–phenolic adhesive formulations in the presence of laccase and proposed the adhesion mechanisms of these preparations to be similar to the mussel adhesive proteins. They tested adhesion between 2 pieces of wood veneer, and conclude that there was no correlation between the number of the OH group on the phenolic compound, or the viscosities and the adhesive strength. In combination to glucose, chitosan wood adhesive properties were investigated [191]. The effects of a Maillard reaction between glucose and chitosan on the resultant chitosan films and the bonding properties of chitosans with different molecular weights were investigated by a tensile shear test. Chitosan and glucose films were dissolved in 1% (v/v) acetic acid and dried at 50 °C. The weight, color, free amino groups, insoluble fraction, and thermal properties of the film changed significantly

Table 2
Bioadhesive applications of chitosan.

Applications	Authors
Haemostasis (Arterial bleeding, wound closure, lung air sealing)	[19,59,75,94,123,152]
Tissue engineering (Nerve engineering, nerve anastomosis, bone and soft tissue gluing, arterial stent, liver cell attachment)	[33,37,54,69,70,108,106]
Drug delivery (Transmucosal and transdermal drug delivery)	[3,33,86,117,180,185]
Antibacterial activity (Chitosan-guar, chitosan-nano silver particles versus *S. aureus* and *E. coli* strains)	[157,183]
Hydrogels (Bioadhesive hydrogels)	[10,68,115,136,141,164]

as the amount of added glucose increased. The dry- and wet-bond strengths were significantly enhanced with increasing glucose addition for low-molecular-weight chitosans. In addition, good bond strength was maintained even in 1% (v/v) acetic acid solution [192]. In the work of Patel et al. [143] the potential of chitosan as wood adhesive was carried out using double-lap shear tests. The best formulation tested was an adhesive composed of 6% (w/v) of chitosan, 1% (v/v) of glycerol, and 5 mmol L^{-1} of trisodium citrate dehydrate. The penetration of the rhodamine-labeled chitosan at 4% (w/v) in the pinewood matrix was also studied using microtome and microscopy techniques to show interactions between chitosan based adhesive and wood. Another application, close to wood adhesion, is reported in the work of Alireza et al. [5]. In the paper industry, in order to enhance the dry-strength properties, and keeping economic and environmental necessity, the chitosan is a good candidate. The experimental results evidenced the potential of chitosan and cationic starch utilization in bagasse paper subjected to hot water pre-extraction. The results of the study revealed that the hand sheets process causes surface arrangement and orientation of chemical groups, which induce a more hydrophobic and basic surface. The acid–base surface characteristics after the addition of dry-strength agents were the same as the bagasse hand sheets with and without hot water pre-extraction. The results showed that the dry-strength agent acts as a protecting film or glaze on the surfaces of bagasse paper handsheets.

In metal adhesive application, the work of Patel et al. [143] described chitosan based adhesives and characterized their shear strength. The desirable features of such adhesives are biodegradability, biocompatibility, non-toxicity, and anti-microbial properties. Various eco-friendly polyanionic polysaccharides, acids, and plasticizers, in single or multiple formulations, were associated with chitosan [142,143]. The resulting crosslinked polymers were glued on some chemically treated aluminum adherends. The shear strength obtained for formulations containing chitosan and glycerol plasticizer was the most significant finding in this study and is equivalent to that obtained with a synthetic adhesive used in industry. Moreover, in the recent work of Cestari et al. [29]. Chitosan was used in cement formulation. In this study, the biopolymer chitosan was used to synthesize a new epoxy/chitosan cement slurry. This slurry was compared to standard cement slurry. A kinetic study of the interaction epoxy/chitosan slurry/HCl was performed to simulate the use of the new slurry in environmental-friendly acidizing procedures of oil wells. The results have pointed out that the main features of the new cement slurry were preserved, even after long-term contact with HCl in aqueous solution. The results of this study underline the excellent features of the new epoxy/chitosan-modified cement slurry for using in environmental-friendly acidizing procedures of oil wells. Finally, in a recent study published by Mati-Baouche et al. [125], the authors have shown and confirmed the potential of the use of chitosan as an adhesive (binder) of plant particles, such as sunflower stem particles, in the development of 100% biobased insulating panels.

6. Environmental assessment and biodegradability of chitosan adhesives

Biodegradation can be defined as the gradual degradation of a material under a controlled mechanism [200]. These mechanisms can involve the use of chemical reagents or biological catalysts, as example for acidic or enzymatic depolymerizations. As reported by Azevedo and Reis [12], the demand for biobased materials with controlled and predictable degradation had led to extensive research on the degradation behavior of a wild variety of biodegradable polymers. Moreover, understanding the factors that control the degradation of biobased materials is critical for the making of degradable polymeric systems (Azevado and Reis, 2004). To our knowledge, few data in the literature have reported the biodegradation of chitosan adhesives. However, various works has reported the possibility to biodegrade various other chitosan forms; the chitosan biodegradability changing accordingly. Thus, chitosan biodegradation can be different regarding its structural form, e.g. solution, adhesive, film, nanogel, and also if chitosan is used (i) alone, (ii) chemically modified or (iii) grafted with other polymers. In this way, enzymatic degradation of thiolated, C-6 oxidized chitosan or genipin-crosslinked chitosan was investigated by using various enzymes [104,150,151]. Many other studies of biodegradations were performed on grafted-chitosan copolymers such as chitosan–phenolics, chitosan–polyacrylamide [20], chitosan–hyaluronan and chitosan–EDC [149], chitosan–poly(ε-caprolactone) [71], chitosan–PVA [42], chitosan-oxidized dextran and chitosan–starch [69], chitosan–dialdehyde cellulose hydrogels [91] or chitosan-alginate and chitosan-carrageenan [50] systems. Note to mention it is crucial to differentiate biodegradation studies on chitosan or on co-polymers grafted on chitosan.

First of all, it has been shown that chitosan can be degraded by various enzymes such as cellulase (3.2.1.4), chitosanase (3.2.1.132), pectinase (3.2.1.15), pepsin (3.4.23.1), papain (3.4.22.2) or amylase (3.2.1.1) (Table 3). Complete enzymatic hydrolysis of chitin and chitosan to free GlcNAc can be performed by chitinolytic enzyme complexes, which are similar to the cellulytic enzyme systems [172]. Note to mention that cellulases are often preferred to chitosanase because of their low costs and supplying facility [32]. Most cellulases (GH-8, and few belong to GH-5 and GH-7) have a bifunctional cellulose-chitosanase activity [201] even if activities and optimum conditions vary with sources. As examples, the cellulases from *Bacillus cereus* D-11 [58] or *Bacillus circulans* [130] possess comparable chitosanase and CMCase activities while the cellulases from *Trichoderma reesei* [76] or *Bacillus* sp. 0377BP [36] show CMCase activity equal to 3–30% of chitosanase activity. Xia et al. [201] have reported numerous chitosanase activities from cellulases or cellulase producing microorganisms. Besides, it has been highlighted that the degrading activity of various chitosanase-cellulases is higher with increasing deacetylation of chitosan, the maximum activity being observed for at least 90% deacetylated chitosan [36,88]. Chitosanolytic cellulases require four or more GlcN pattern and cleave bonds with an *endo*-type

Table 3
Some examples of the wild heterogeneity of enzymes able to degrade chitosan (C), modified chitosan (MC) and copolymers-chitosan (CPC).

Enzymes	EC	Mode of action	Potential substrate	References
β-*N*-acetylhexosaminidase	3.2.1.52	Hydrolysis of terminal non-reducing sugar	β-D-hexosamineNAc, chitin, C, CPC	[173]
Cellulase	3.2.1.4	*Endo*-type cleavage, few *exo*-type (highly active for insoluble substrate), few *exo*-β-D-glucosaminidase	C, MC, CPC, CMC[1], Avicel	[118,201,91,150]
Cellobiohydrolase	3.2.1.176	Hydrolysis of reducing end β-D-Glc	C, MC, CPC	[201,150]
Chitinase	3.2.1.14	Random hydrolysis GlcNAc	Chitin, C, CPC	[173]
Chitosanase	3.2.1.132	*Endo*-hydrolysis GlcN-GlcN, few recognizing of GlcNAc-GlcN or GlcN-GlcNAc	C, CPC	[77,165,89,186]
Exochitosanase	3.2.1.165	*Exo*-hydrolysis of GlcN-GlcNAc from non reducing end	Chitin, C, CPC	[57]
Lipase (except human)	–	–	C, CPC	[198]
Lysozyme	3.2.1.17	Mainly hydrolysis of GlcNAc-GlcNAc	Chitin, C, CPC	[81,149]
Papain	3.4.22.2	Degradation of long chains, only GlcNAc-GlcN	C, CPC	[72]
Pectinase	3.1.1.15	GlcN-GlcN supposed pattern	C, MC, CPC	[178,167,93,150]

[1] CMC: carboxymethycellulose.

mechanism, *e.g.* $(GlcN)_6 \rightarrow (GlcN)_3$ plus $(GlcN)_3$ or $(GlcN)_4$ plus $(GlcN)_2$. On the other hand, most chitosanases specifically degrade chitosan and not chitin or cellulose [44,170,89]. To date, a large number of chitosanases have been reported from several bacteria, fungi, cyanobacteria or plants [186]. Theses enzymes belong to five glycoside hydrolase families, *i.e.* GH-5, GH-8, GH-46, GH-75 and GH-80, and can hydrolyze links in chitosan. Thus, chitosanases are classified into three distinct subclasses [186]. Chitosan is also degraded by various lysozymes, which are present in various plants and animals. Lysozymes are widely used for chitosan degradation especially for its application on drug delivery and tissue engineering in humans [25]. It has been shown a basal number of acetyl groups (degree of deacetylation lower than 80%) and the free hydroxyl group at C3 of sugar residues are required to obtain good hydrolysis rates [188]. Lysozymes contain a hexameric binding site and hexasaccharide sequences with 3 or more acetylated units which contribute mainly to the initial degradation rate of sufficiently *N*-acetylated chitosan. More recently, the biodegradation of chitosan-based films was performed by enzymes at *in vivo* conditions. Thus, Freier et al. [54] have performed long-term experiments using physiological pH and enzymes at human body concentrations and obtained the best depolymerization yields for 40–60% *N*-acetylated chitosan.

Overall, the specific degradation of chitosan by lysozymes is a beneficial aspect for medical, drug-release and tissue engineering applications. Chitosan and chitosan-made products are also susceptible to pectinase which are produced by a number of bacteria, yeast, fungi, protozoa, insects, nematodes and plants [1]. In this way, investigations have been done to improve the activity of commercial pectinase by modifying the performance of the enzymes [178]. Finally, other enzymes have been reported for their ability to hydrolyze chitosan, such as hyaluronidase [98], papain [72], amylase [207], lipase [198] and more recently liRase (lipoamide reductase) and collagenase [97].

In a general point of view, it seems clear that chitosan and derivates can be degraded by various different enzymes, which expands the work to various biodegradation ways. The use of microorganisms producing chitosanolytic enzymes to degrade *in situ* chitosan-made products [158] is

an interesting topic which is blooming, especially for assessing the potential of chitosan as eco-friendly biodegradable polymers for adhesive, coating or drug-releasing uses.

As already presented above, chitosan has gained lot of attention as biomaterial in several field such as for example: (i) wood/metal adhesives and mucoadhesives and, (ii) tissue engineering applications; owing to its large-scale up availability, its low cost, biocompatibility and biodegradability [86]. The use of adhesive bonding in industry has notably increased in recent years and most of producers adhesive try to more and more integrate the environmental impact notion into their manufactured products. In this context, greener alternative is necessary. One of the most important advantages of using biobased polymers such as chitosan for adhesives manufacturing should be it relative low impact in environmental problems unlike chemical adhesives that are more polluting. In an eco-designing point of view, when industrial need to incorporate an ecological innovation in order to implement a novel biobased adhesive, the good knowledge of the environmental effect of these products is primordial [46]. As mentioned by Lorenz [116], life-cycle assessment (LCA) is well-defined as a comprehensive methodology largely used to estimate and evaluate the environmental impact of compound or process all over its whole life cycle according to ISO 14044. Generally speaking, the best typical crop of the environmental impact of a product must take into account the environmental courses all over the whole product's life which include the emission to land, water and air as well as the energy and material balance of product resources [179,195]. It was well accepted by the international community that a complete LCA during the whole life cycle of a compounds from the extraction of natural raw materials following by their modification/transformation/designing/manufacturing into a product, through the practical use of the product and finally the end of life circumstances such as disposal or recycling, was considered as the "cradle to grave" concept [39]. This notion implicated not only one single parameter but a succession of analysis throughout product life cycle. Narayan [133] has recently discussed the use of biobased material founded on LCA. It was particularly reported that in comparison to petroleum based materials, biobased materials could significantly reduce the energy/environmental balance
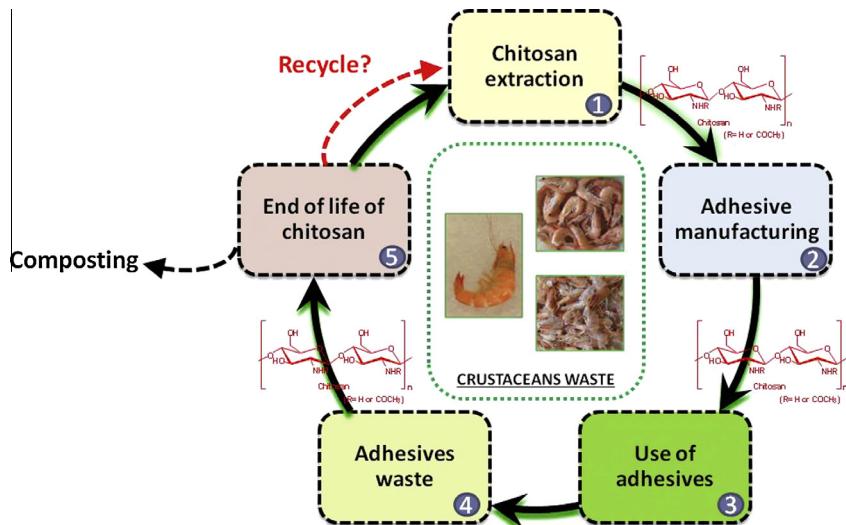
Fig. 4. Schematic representation of the Life Cycle thinking approach for chitosan-based adhesive.

impact. According to Narayan [133], it was found that bio-based materials such as adhesives engineered from biomass feedstocks should prospectively play an increasing major role in our consumer society which is in perpetual search of sustainable and environmentally friendly materials. Nevertheless, by comparison with lot of LCA studies which evaluated chemical products [195], few LCA approaches have evaluated biobased material with respect to economical and environmental profits [61,112]. In fact, up to now, LCA has been essentially implemented to the environmental impact estimation of pharmaceutical drugs and biofuel production [9,38,105,166,45,159]. As far as we know, there is no data available in literature for the LCA of chitosan adhesive. Moreover, one of the most important limitations that may occur in this study of environmental impact of adhesive chitosan seems to be the real lack of well-defined information to compare and correlate all the steps of processes during the entire cycle life of chitosan from extraction, use as adhesive and through end-life of product. By way of comparison, it should be interesting to analyze the studies realized by Leceta et al. [110–112] on the environmental assessment of chitosan-based biomaterial in order to propose and try to simulate a cycle life assessment scenario for chitosan as adhesives. In their work, Leceta et al. [110,111] seek to estimate the real environmental impact of manufacturing chitosan from waste crustacean to biobased films. They have analyzed the different steps of the processes and provided data for comparing chitosan to other chemical compounds. Then, Leceta et al. [110,111] have investigated a comparative environmental assessment between a new biodegradable chitosan based film and a commercial food packaging film based on polypropylene. Three mains stages have been evaluated: the chitin extraction and chitosan production; the film manufacture and the end of life of the biomaterial. Obviously, it was shown that polypropylene based film presented higher impact than chitosan-based films in carcinogens and fossil fuels. It was clearly confirmed that first, polypropylene extraction stage was the most pollutant and

energy consumer and secondly, the environmental problem associated to carcinogens was mainly link to the end of products. Moreover, it is important to note that chitosan-based films was described as higher environmental burden in land use, minerals categories and respiratory inorganics. Effectively, as related by authors, environmental damage associated to respiratory inorganics was commonly associated to the acetic acid used to dissolve and manufacture the chitosan film. But, in a more dramatically way, the main pollutant compounds implicated in the negative impact in mineral category are the hydrochloric acid and sodium hydroxide currently employed during the chitin/chitosan extraction. Finally, it should not be forgotten the glycerin used as plasticizer in film manufacture. This additive considered as a by-product from biodiesel field, is the main responsible agent to take into account in the negative impact of land use. Nonetheless, an environmental benefit of chitosan is the end of life stage because of the biodegradation of chitosan based material which permits composting of chitosan as its end life [112] exhibiting then a greatly positive result on the environment in comparison with the classical end of life intended for plastic material. Thus, by analogy with these LCA studies on chitosan films, needless to say that we could envisage the same life cycle assessment scenario with the use of chitosan as adhesives since the same process stages are operated from the extraction (using hydrochloric acid/sodium hydroxide) to manufacture of adhesive (using acetic acid and glycerol). Consequently, based on the result demonstrated by Leceta et al. [110–112], a schematic diagram of life cycle could be proposed as presented in Fig. 4. This diagram details the main stages of the production of chitosan-based adhesive from the crustaceans waste to the end of life of adhesive. In conclusion, as well related by Hatti-Kaul et al. [67], there is strongly need to develop sustainable and innovative biobased material in order to shift the resource from fossil to natural and renewable raw material. Nowadays, environmental and economical aspect must be considered when a new adhesive is being designed. Therefore, a preliminary

environmental assessment approach should be mandatory to develop biobased sustainable adhesives. This biotechnological challenge will certainly focus on the choice of natural adhesives such as chitosan and derivatives so as to positively influence the environmental benefits and the life cycle performance.

7. Conclusion

To conclude, chitosan has become a popular biopolymer in the medical fields because of its unique properties in the world of biopolymers. However the analysis of literature focusing on its mechanical characteristics and the development of its industrial production clearly showed the interest of other scientific communities for this polysaccharide. In this way the analysis of its performances as adhesives, as binder and as film clearly showed that it could be competitive with some fossil resources. Nevertheless, some progresses have to be done in the processes used for its obtaining from bioresources with the objective to limit the costs of these processes and to limit their impact on health and environment.

Acknowledgements

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